

EXPERIMENTAL STUDY OF CERTAIN ELECTRONIC BANDS OF CO₂

A DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE
UNIVERSITY OF MICHIGAN

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JAMES F. DUNCAN

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ABSTRACT

The electronic bands of CO₂ lying near 2880A and 2895A are described and a method given for photographing them under very high dispersion. Three good plates were obtained which gave concordant results when examined with a comparator and with a Moll microphotometer. The fine structure, the probable emitter of the bands, and their relation to other bands of the spectrum are discussed.

IN A series of band-groups attributed to carbon dioxide by Duffendack and Fox¹ and later described by Fox, Duffendack and Barker² two bands located near 2880A and 2895A appeared to be different in structure. These bands which are of greater intensity than the others of the system, appeared under medium dispersion to be similar in form and to consist of a positive, a negative and a zero branch. The purpose of the present investigation was to examine these bands under very high dispersion with a view to resolving their fine structure.

APPARATUS AND METHOD

In order to investigate these bands it was necessary to obtain much greater dispersion than is possible with the E1 Hilger spectrograph. Preliminary tests made on a 21-foot concave grating gave a dispersion of 1.2A per millimeter in the second order which seemed sufficient for the purpose. The grating, ruled by J. A. Anderson at Johns Hopkins University, contains 14,400 lines to the inch.

The source consisted of a low-voltage arc-discharge in a continuously flowing stream of pure carbon dioxide. The discharge tube, which was made of Pyrex glass with a quartz window was connected with the gas reservoir and the pumping system in such a way that the direction of the gas stream was from the anode to the cathode (i.e. opposite the direction of the electric current). This arrangement provided that the discharge products were pumped off as soon as they were formed thus insuring pure carbon dioxide in the discharge space. The cathode consisted of three oxide-coated spirals of platinum wire connected in parallel. These were placed so as to leave a space of two or three millimeters between the cathode and the anode. This served to localize the discharge. The filament was heated by current supplied from storage batteries. The anode was a nickel box which surrounded the cathode except on the side next to the quartz window.

¹ O. S. Duffendack and G. W. Fox, *Astrophys. J.* **65**, 214 (1927).

² G. W. Fox, O. S. Duffendack and E. F. Barker, *Proc. Nat. Acad. Sci.* **13**, 302 (1927).

The carbon dioxide used in this investigation was taken from commercial tanks and, after being purified by passing through tubes of calcium chloride and phosphorus pentoxide and by freezing in a liquid-air trap, was stored in a glass reservoir. By means of a grooved stop-cock connecting the reservoir with the discharge tube it was possible to regulate the rate of passage of the gas into the tube. The pumps kept the gas flowing through the tube at a steady rate and at constant pressure, and thus fresh carbon dioxide was continually supplied at the arc.

The tube was operated at about one-tenth millimeter pressure. The filaments emitted most efficiently at currents ranging from five to ten amperes when the potential across the tube was about sixty-five volts. This gave an arc current of from six to fifteen milliamperes. It was found difficult to operate the tube with the arc current above fifteen milliamperes without producing dissociation of the carbon dioxide together with flares.

For photographic plates Cramer's Hi-speed plates were found most successful. Cramer's contrast plates were tried but were found impractical since they required a longer exposure and since the length of exposure in the case of the Hi-speed plates was already from fifty to one-hundred hours. Longer exposures than these could not be made since the temperature of the room could not be kept sufficiently constant.

The entire apparatus was set up in a room thirty feet under ground and great care was taken to house it in such a way as to shield the grating from the heat generated by the source and from all stray light. It was found that the temperature of the grating could be kept constant to within one-half degree centigrade throughout a period of one-hundred hours.

RESULTS

Three records were obtained on which the fine structure was clearly resolved over a considerable distance. These plates were measured on a precision comparator and the frequencies of the lines were found by comparison with standard iron lines. Table I contains a composite record of the three plates together with eye estimates of intensities. A question mark follows those values for which the individual settings differed by more than 0.01 millimeter, that is, by about 0.01 Å.

One of the records, taken in March, was obtained under the most favorable conditions, that is, with a temperature change of only one-tenth degree centigrade. It was, therefore, taken as standard for the absolute values of the frequencies of the lines. The other two records taken in May and July show a slight shift of all the frequencies towards the red. This shift is undoubtedly due to a temperature change of the grating caused by large temperature changes of the atmosphere outside. Therefore, certain characteristic lines of the spectra, namely, $\nu = 34,512.430$ and $\nu = 34,673.287$, were made to coincide on the three records and corrections were applied to all the other lines thus bringing the three records into good agreement.

Microphotometer records were made from these plates and the peaks on the microphotometer records of the three plates were readily identified with

TABLE I. *Composite record of wave-numbers of lines in the CO₂ bands.*

ν	I	ν	I	ν	I	ν	I
34,441.199?	00	34,498.388	2	34,561.974?	0	34,667.807	0
444.699?	00	499.543	1	580.434	6	669.309	0
447.680	0	500.746	4			673.287	10
449.957	1	501.889	3	607.482	1	678.918	4
452.463?	00	503.044	3	608.820?	2	682.203	10
454.338?	00	505.533	2	610.034	3	684.330	7
455.525?	00	507.225	5	612.409	3	685.461	3
458.126?	00	508.475	0	614.750	1	686.945	5
460.228	0	509.715?	00	616.776	2	687.869	5
463.164	0	510.977?	00	619.150	2	688.808	2
465.753	0	512.430	10	621.355	2	697.864	1
466.894	0	516.603	3	623.838	2	700.143	1
467.777?	00	518.126	6	626.080	3	702.013	1
469.627	1	520.736	10	629.522	3	704.060	1
470.994	0	525.009	7	632.978	3	705.870	2
472.000?	00	526.833	7	635.893	3	707.796	2
474.333?	00	534.901	2	638.402	3	710.254	2
476.855	2	536.498	2	641.065	3	712.508	2
479.622	4	537.836	2	643.406	3	714.639	2
482.265	4	539.199	2	646.072	2	717.185	2
484.679	4	540.522	3	648.642	2	718.980?	0
486.119	3	542.111	3	651.585	3	720.146	0
487.178	4	544.137	3	653.554	3	722.388	0
488.260	3	546.025	3	655.884	3	724.802?	00
489.331	3	547.936	3	657.781	4	727.687?	00
490.426	4	548.883	2	658.804	2	729.475?	00
491.462	3	550.012	3	659.957	4	731.381	0
492.389	3	552.019	2	661.110	3	739.960	5
493.520	4	553.688	2	663.095	3	741.392	5
494.638	3	555.388	0	664.296	3	768.742	0
495.603	3	558.073	0	665.462	2	773.313	7
496.996	2	560.142	0	666.484	1	801.210	3

each other and with the measurements of the comparator. Fig. 1 is a microphotometer record of a spectrum plate taken after the microphotometer had been carefully adjusted to render negligible the effect of plate grain. This was accomplished by lengthening the line of light on the photographic plate so that it extended over many grains of the plate. Records similar to Fig. 1

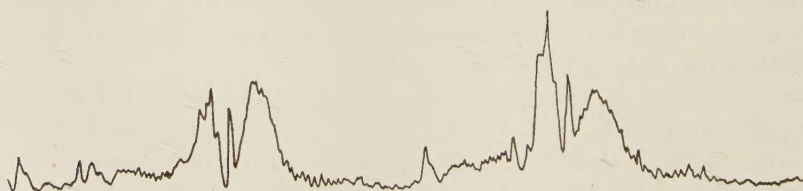


Fig. 1. Microphotographic record of band structure (retouched).

but greatly extended along the horizontal axis were used for measurements.

In order to get a clear idea of the structure of the bands it has been found convenient to represent the photographic plate by means of a graphical chart of the lines (Fig. 2) and to compare this with the microphotometer records. Some features which are not apparent on the one type of record appear prominent on the other.

In describing the general features of the bands it is possible to state immediately that the two bands with centers at $\nu = 34,512.430$ and $\nu = 34,673.287$, respectively, are similar in structure. Each has a form suggesting a positive, a negative and a zero branch. In the description which follows, these terms will be used with the understanding that these regions may not, however, be true positive, negative and zero branches.

The zero branch in each case appears as a single, very sharp and very intense line.

The negative branch is quite regular in appearance. While the lines appear to extend up to the zero branch their intensity in this region is so small that measurements on their positions can not be made with any great certainty. Extending from the zero branch through a range of about 25 wave-numbers the lines are closely spaced. While the spacing is somewhat irregular it is of the order of 1.1 wave-numbers. Extending on beyond this the spacing

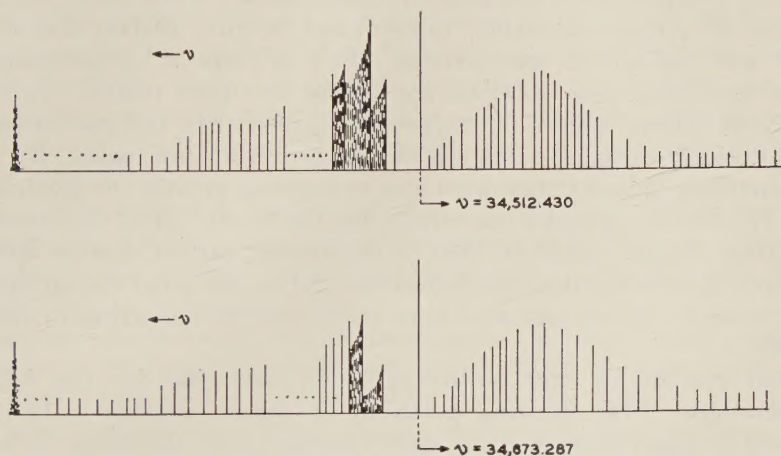


Fig. 2. Diagrammatic chart of lines of the two bands.

has a value of the order of 2.5 wave-numbers. The position of maximum intensity lies at about 14 wave-numbers from the center and lines are found as far out as 70 wave-numbers from the center of the band.

The positive branch presents an appearance very different from that of the negative branch. No fine structure is visible through a range of 5.6 wave-numbers out from the zero branch. (One plate shows a line at 4.2 wave-numbers from the center of the band.) At 5.6 wave-numbers from the center a strong edge or line is found having an intensity of about one-third that of the zero branch. At about 9 wave-numbers from the center there is a sharp edge or line of about the same intensity as that of the zero branch. In one band it appears somewhat greater than that of the zero branch, in the other somewhat less. (See Fig. 1) This difference in the two bands may be due to the fact that the resolution in the band where the intensity is greater is not as good as it is in the band where the intensity is less. Throughout this region extending out to about 10 wave-numbers from the center there

is fine structure having irregular spacing but of the order of magnitude of one wave-number. Out farther the spacing increases to about twice this amount. At about 68 wave-numbers from the center of the band the lines end in a fuzzy edge.

Beyond the end of the positive branch of the band whose center is at $\nu = 34,673.287$ three lines are found at $\nu = 34,768.742$, $34,773.313$ and $34,801.210$. These do not seem to have any relation to the bands.

DISCUSSION

None of the lines of the band systems photographed by Fox, Duffendack, and Barker² is absorbed in normal carbon dioxide, thus showing that the normal state of the molecule is not involved in the transitions giving rise to these spectra.

In a later paper Duffendack and Smith³ did some work towards determining the excitation energies for these bands. They found that with mixtures of carbon monoxide, oxygen and helium, carbon dioxide was formed and the spectra were excited. In a mixture of carbon monoxide, oxygen and neon they obtained the bands but more faintly, while in a mixture of carbon monoxide, oxygen and argon they did not obtain the bands although carbon dioxide was formed as in the other cases. By means of an auxiliary filament they were able to increase greatly the electron current. This did not enhance the carbon dioxide bands. They concluded that the carbon dioxide bands are due to the ionized carbon dioxide molecule, and that there was simultaneous ionization and excitation of the carbon dioxide molecule by helium and neon ions, by excited helium and neon atoms or by both.

Their conclusions may be strengthened somewhat by the following considerations. The ionizing potential of carbon dioxide is 14.3 volts. One volt is equivalent to 8100 wave-numbers and, therefore, 34,512.430 wave-numbers (the center of one of the bands) are equivalent to about 4.3 volts. If, then, the spectra are due to ionized carbon dioxide the excitation potential must be at least 18.5 volts. This lies near an excitation potential of helium, 19.77, so that one should expect a comparatively strong excitation in the presence of excited helium. In neon the ionization potential is 21.5 volts in which case the probability of exciting the carbon dioxide ion would be less. In the case of argon, the ionization potential of which is 15.5 volts, there could not be excitation of the carbon dioxide ion. We may, therefore, conclude that the bands under consideration are due to the carbon dioxide ion.

It was intimated above that the respective regions of these bands might not be true positive, negative and zero branches. The reasons are as follows: The positive and negative branches do not show the requisite symmetry or complementary nature and the zero branch seems far too sharp to represent a region of many closely spaced lines.

³ O. S. Duffendack and H. L. Smith, *Phys. Rev.* **34**, 68 (1929).

The question of what relation exists between the two bands under discussion and the groups of bands discovered by Duffendack and Fox extending from about 2800A to nearly 5000A must be left without a complete answer, at least until the groups have been photographed under greater dispersion. Very faint traces of one of the stronger groups were found on the plates obtained in this investigation but it was impossible to obtain them with sufficient intensity for measurement. A much stronger source will have to be devised before these groups can be photographed with the 21-foot grating.

The fact that both types of bands have always been found together and that no difference in excitation potential was noted by Fox, Duffendack and Barker² makes it probable that both types are due to a single electronic transition with the various groups due to particular vibrational transitions. Since the two bands investigated in the present work have an essentially different structure from the rest it is suggested that they may be due to a different type of vibration transition. In a linear model of the carbon dioxide molecule there are three independent frequencies of vibration and consequently the vibrational structure will be much more complex than in the case of a diatomic molecule and the different classes of vibrational transitions will give different fine structure.

Fox, Duffendack and Barker² fitted the leading edge of a number of the groups into a series with second differences nearly constant. However, not all the groups could be fitted into this scheme. The bands near 2880A and 2895A do not fit into this series.

Whatever may prove to be the explanation of these band groups, it seems certain that the bands near 2880A and 2895A are independent and form a system by themselves. This system may be due either to a transition from a higher electronic state containing a single vibrational level to a lower electronic state which contains two vibrational levels, or to a transition from a higher electronic state of two vibrational levels to a lower electronic state containing one vibrational level, since only the two bands appear.

In conclusion the writer wishes to express his appreciation for the kind assistance and continued interest of Professor O. S. Duffendack who directed this research and for the many helpful suggestions of Professor D. M. Dennison.



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